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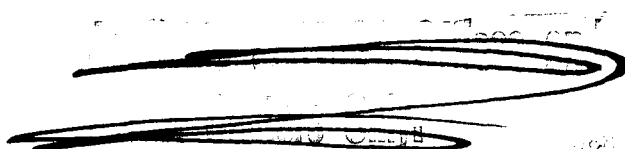
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by

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The major research activity of this project has been concerned with the fundamental acts of cross-linking polymers and the manner in which the efficiency of cross-linking and the properties of the resultant isotropic network depend on the state of the polymer at the time the cross-links are introduced. The studies to date have been restricted to natural rubber and linear polyethylene with major attention being given to the latter polymer. Cross-links can be introduced into both these polymers by means of high energy ionizing radiation, and we have been utilizing x-rays from a three m. e. v. Van der Graaf for this purpose.

The two states of polymeric systems which are of most obvious interest for the above purposes are the crystalline and amorphous states. However, our experimental results have indicated that further distinction is required, since the efficiency of cross-linking is affected significantly by the finer structural details in each of these states. For example, in the amorphous state distinction needs to be made between undeformed and deformed systems. For crystalline polymers the same distinction needs to be made. In addition, however, the level of crystallinity is important as is the molecular nature of the crystallites, i. e. the chain disposition within the crystallites. This latter statement is made since the results reported below indicate a significant difference in the mode of network formation between well crystallized samples prepared from the bulk molten polyethylene and the "single crystals" formed from dilute solution crystallization. When comparing cross-linking and network formation between the different states the temperature at which the polymer is irradiated should be the same. If not, cognizance must be taken of

any inherent temperature effects which are independent of the state. Since the latter procedure is theoretically difficult, we have developed methods where the irradiation of crystalline polyethylene and crystalline natural rubber can be compared at the same temperature with the irradiation of the completely amorphous polymer.

(We report first the results of irradiating both highly crystalline and completely amorphous unfractionated linear polyethylene (Marlex-50) at $130^{\circ}\text{C}.$) From studies of the crystallization kinetics from the melt of this polymer, it is found that a highly crystalline sample and a completely amorphous sample can be irradiated at the same temperature $130^{\circ}\text{C}.$ The dose rate utilized, 3.5 megarads 1 hr., allows the supercooled liquid to be maintained at 130°C for an adequate length of time. In a complementary experiment, crystallization can be conducted independently at this temperature. About forty days are required for the crystallization process to be essentially complete. The crystalline specimens can then be irradiated at $130^{\circ}\text{C}.$ It is found that although the gel-point occurs at about the same dosage for both types of samples the partitioning between sol and gel with further irradiation is quite different. Gel is formed more rapidly in the crystalline samples. The isotropic swelling in xylene of networks formed in both states was measured at $140^{\circ}\text{C}.$ When compared at the same fraction of gel formed (not at the same irradiation dose) networks formed from the crystalline polymers swell a greater amount. According to theoretical concepts, the elastic modulus of the isotropic networks should show a similar difference.

In order to understand and analyze the effects described above in greater detail, a program has been undertaken of the irradiation of molecular weight

fractions of linear polyethylene. In the first phase of this program, molecular weight fractions of $M=1.1 \times 10^5$, 6.2×10^5 and 1.25×10^6 have been studied. Other molecular weight fractions are being obtained in sufficient quantity from an independent fractionation program. All three fractions were irradiated at 133°C in the amorphous states. It is the first time to our knowledge that such experiments have been performed on molecular weight fractions. The dosage required for gelation depends on molecular weight in agreement with classical theory. The partitioning of the samples between sol and gel also follows theoretical expectations for a fraction and differs quite substantially from that of the unfractionated polymer. It is noted, however, that even for the fractions a small proportion of sol remains even at high irradiation dosages. One fraction, $M=6.25 \times 10^5$ available in sufficient quantity, was crystallized at 130°C for 50 days and subsequently irradiated. The gel-point occurred at a slightly lower dosage than the amorphous polymer; the partitioning between sol and gel occurred rather sharply with irradiation. No detectable sol portion remained even after relatively large dosages.

The swelling ratios of the networks formed from amorphous polymer depend on molecular weight, with the swelling ratio decreasing with increasing molecular weight at the same cross-linking density. This can be attributed to imperfect network formation with the effective number of cross-links, at a fixed cross-linking density, increasing with increasing molecular weight. The swelling ratios of the network formed from the crystalline molecular weight fraction is greater than that of the network formed from the corresponding amorphous polymer. The investigations with fractionated material is being continued. The significant results to date can be summarized as follows. The rate of cross-linking with dosage is more effective in bulk crystallized linear

polyethylene than in the corresponding amorphous polymer when the irradiation is conducted at the same temperature. However, the swelling ratio of isotropic networks formed from crystalline polymer is greater than that of amorphous networks when compared at dosages corresponding to the same fraction gel. Since the cross-linking density is the same in both cases, this difference in behavior is attributed to the different chain configurations in the two cases at the time of network formation.

The other crystalline state of linear polyethylene which we have studied in some detail is that of ("single crystals" precipitated from dilute solutions of xylene.) In agreement with other reports in the literature we find that for unfractionated polymer the gel-point, at room temperature, occurs at a much greater dosage than for the usually crystalline polymer at the same temperature. This result is usually explained by the regular folded chain configuration of the "single crystals" with a predominance of intramolecular cross-links being formed. However, we have observed a profound effect of the molecular weight on both the dosage required for gelation as well as the partitioning of the sample between sol and gel with increasing irradiation. For two fractions, $M = 1.1 \times 10^5$ and 1.25×10^6 , the gel-point is found to be 8.5 and 3.0 megarads respectively. Although the difference is not in accord with the theory of the random intermolecular cross-linking of random chains, the fact that there is such a significant effect of molecular weight raises the question as to the nature of the detailed chain arrangement within the single crystals. For, if as it has been postulated, intermolecular cross-links occur only between individual lamella then the molecular weight should have no effect on the dosage required for gelation. Experimentally, this work is being continued with other fractions and a theoretical interpretation of the results is being developed.

By cross-linking a film of unfractionated linear polyethylene (Marlex-50) just to the gel-point it is found that it can be stretched twenty times its original length in the amorphous state above its melting point. On subsequent cooling to room temperature, a highly axially oriented crystalline structure is developed as indicated by wide angle x-ray diffraction. The density of the specimen, 0.96, is indicative of a high level of crystallinity. Efforts are being made to increase the density and level of crystallinity of such specimens by annealing experiments and by isothermal crystallization at higher temperatures. In the meantime, experiments have been initiated to investigate both the relative efficiency of cross-linking the highly axially oriented specimens relative to the undeformed but crystalline specimens, as well as the properties of the resultant networks.

Studies involving natural rubber are being continued. The major current interest is quantitatively determining the effect of uniaxial orientation (without crystallization) on the relative efficiency of cross-linking.